Photochemistry of Complex Ions. XII. Photochemistry of Cobalt(III) Acidoammines

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Abstract: The photolysis of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5(H_2O)^{3+}$, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5Cl^{2+}$, $trans$-$Co(en)_2Cl_2^+$, and $trans$-$Co(cyclam)Cl_2^+$ in the wavelength region of the ligand field bands is reported, using a continuous wave Argon laser as light source. At 488.0 nm, quantum yields for Co(II) production by redox decomposition are negligible compared to those for ammonia and X^- aquation, which range from 10^{-4} to 5×10^{-3}. For the acido-ammines, ϕ_{NH_3} dominates over ϕ_{X^-}, and in the case of the chelate complexes, only chloride aquation occurs; $trans$-$Co(en)_2Cl_2^+$ is 72% stereoretentive to give the $trans$-chloro aquo complex, while $Co(cyclam)Cl_2^+$ photoaquates with 100% stereoretention. It is believed that the low quantum yield values reflect enhanced radiationless deactivation rates, relative to the corresponding Cr(III) complexes, rather than reduced excited state chemical reactivities. The qualitative photochemistry partly conforms to the photolysis behavior of Cr(III) complexes but differs in detail; for example, the stereochemistry of the products indicates that important differences in excited state reaction mechanisms are present.

The photochemistry of Co(III) coordination compounds has been studied quite extensively.[1,2] The emphasis has been somewhat different, however, from that of the perhaps even better studied Cr(III) family. With the latter, attention has been focussed heavily on the photochemistry in the wavelength region of the first and second ligand field (L_1 and L_2) bands. Photosubstitution occurs in generally good quantum yields (with one notable exception)[3] and is often antithermal in reaction mode. The collection of observations has allowed generalizations in the form of empirical rules,[4] which in turn have received some recent theoretical attention.[5-7] Finally, the photosubstitutions often appear to be stereospecific in an antithermal manner; thus, $trans$-$Cr(en)_2Cl_2^+$ photolyzes primarily to cis-$Cr(en)_2(H_2O)Cl^{2+}$ while thermal aquation yields the trans isomer[8] (see also ref 9 and 10 for related examples).

The observed photochemistry of Co(III) complexes has in contrast been primarily for wavelengths in the region of the first charge transfer (CT) band and is largely one of redox decomposition[1,2] (see also, for example, ref 11). Relatively little attention has been paid to photochemistry in the L_1 and L_2 wavelength regions, perhaps mainly because the common ammine complexes are not very photosensitive unless some CT character seems present, as indicated by a larger than usual extinction coefficient, in which case photoredox decomposition again may occur in good yield. The aquation which may also occur in the above situation has been attributed to cage reaction following homolytic bond fission and thus may not represent a primary photosubstitution process.[12a] Examples of the photoinsensitivity of normal ligand field bands consist mainly of $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5Br^{2+}$ for which ammonia, ethylenediamine, and halogen aquation yields, respectively, are reported in the range of 10^{-3} to 10^{-4} or less,[1,2] with virtually no information as to whether more than one aquation mode is present in the latter case. There has

(1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1971.

(2) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(3) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 5581 (1971).

(4) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

(5) J. I. Zink, *Inorg. Chem.*, **12**, 1018 (1973).

(6) M. Wrighton, *Mol. Photochem.*, **5**, 165 (1973).

(7) C. H. Langford and N. A. P. Kane-Maguire, *Proc. Int. Conf. Coord. Chem.*, *14th* (1972).

(8) A. D. Kirk, *J. Amer. Chem. Soc.*, **93**, 283 (1971).

(9) M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

(10) P. Riccieri and E. Zinato, *Proc. Int. Conf. Coord. Chem.*, *14th* (1972); E. Zinato and P. Riccieri, *Inorg. Chem.*, **12**, 1451 (1973).

(11) (a) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 2470 (1973); (b) E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76**, 2492 (1972).

(12) (a) See A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970). (b) We will arbitrarily define as photoinert a species for which the total quantum yield is less than 0.01 at the wavelength in question.

been no basis for judging whether photolysis rules such as those for Cr(III) complexes may exist.

The present study was undertaken to remedy this deficiency in information. It was possible, of course, that the photoinertness[12b] of Co(III) ammines would turn out to result from low efficiency photocatalyses of normal thermal reactions and to have little intrinsic interest. We felt, however, that these low yields more likely resulted from relatively rapid radiationless deactivation in the case of Co(III) excited states and that the ligand field photochemistry would turn out to be quite specific in nature. As noted in a preliminary communication,[13] we do find a varied photochemical behavior, often antithermal, whose richness promises to rival that of the analogous Cr(III) species. We now report our detailed results.

The present study has greatly been facilitated by the use of a continuous wave laser source. Such lasers provide highly monochromatic beams of intensity and degree of colimation that allow much higher than usual absorbed radiation fluxes (einsteins per (liter second)). A secondary purpose of the study has been to demonstrate the value of laser over conventional photolysis sources.

Experimental Section

Materials. The various complexes were prepared according to standard literature procedures: $[Co(NH_3)_6](ClO_4)_3$,[14] $[Co(NH_3)_5-(H_2O)](ClO_4)_3$,[15] $[Co(NH_3)_5F](ClO_4)_2$,[16] $[Co(NH_3)_5Cl](NO_3)_2$,[17] trans-$[Co(en)_2Cl_2](NO_3)$,[18] and trans-$[Co(cyclam)Cl_2](NO_3)$,[19] where cyclam denotes 1,4,8,11-tetraazacyclotetradecane. Analytical quality reagents were generally used.

Photolysis Procedures. Solutions to be photolyzed were 10^{-3} to 10^{-2} M in complex and normally 10^{-2} M in perchloric, nitric, or hydrochloric acid (the latter acids were used if the solubility of the perchlorate salt of the complex was not sufficiently high). In the case of the pH dependence studies, solutions of pH 4 and 5 were made up with the use of acetate buffering with the total acetate concentration about 0.1 M. Solutions of pH 7, 8, 9, 10, and 11 were buffered with carbonate buffers, of total carbonate concentration about 0.1 M. The pH 7 and 8 solutions were verified before each use by means of a Beckman pH meter; the former could be maintained during the irradiation period with difficulty and only by slowly bubbling carbon dioxide through the solution.

Solutions of pH 6 or higher would become cloudy on irradiation due to cobalt hydroxide formation. To prevent this, they were made about 0.01 M in EDTA (ethylenediaminetetraacetate), which complexed the Co(II) produced and prevented such precipitation. Separate tests showed that the presence of the EDTA did not interfere with the analytical procedures.

Many of the irradiations were carried out with the use of jacketed, thermostated 10-cm Perkin-Elmer micropolarimeter cells of either 0.82- or 5.0-cm³ capacity. Larger volume irradiations were made with the use of standard 10-cm Cary spectrophotometer cells of 27-cm³ volume, thermostated by means of a previously described temperature-controlled block.[20] Unless otherwise specified, irradiation temperatures were 25 ± 0.5°. Even with the smallest microcell, checks with an in situ thermistor probe showed that at 1 W laser beam power levels the thermostated jacketing held the temperature rise during irradiation to about 0.2°.

The light source was a continuous wave Argon laser (Coherent Radiation Model 52-B) with internal wavelength selection set at either 488.0 or 514.5 nm. The per cent light absorption in the irradiation cell was determined by the absorption spectrum of the solution as measured on a Cary Model 14 spectrophotometer. Photolyses were carried out to less than about 10% total reaction so as to avoid corrections for changes in absorbed light intensity during photolysis, internal filter effects, and secondary photolysis (the laser beam itself was very stable in intensity). For the same reason, with two exceptions, concentrations were adjusted so that no more than about 80% absorption of incident light occurred in the 10-cm path length of the irradiation cell. To facilitate the chloride ion analysis, solutions of $Co(NH_3)_5Cl^{2+}$ were of concentrations such that 99% of the incident light was absorbed. The solutions of trans-$Co(en)_2Cl_2^+$ were likewise concentrated for the product isomer ratio study. Whenever such highly absorbing solutions were used the cell containing the solution was agitated at frequent intervals. The cross section of the laser beam was about half of that of the smaller micropolarimeter cell and was unmodified when this cell was used. To avoid the need for stirring in the case of the larger cross section cells, the beam was expanded by means of a lens, to occupy about two-thirds of the cell window area.

Light intensities (einsteins per centimeter) incident on a cell window were determined by Reineckate actinometry[20] which, after correction for window (and any lens) reflection,[20] gave values about 20% less than those calculated from the power meter readings of the laser unit (we thus observed that not all of the light intensity recorded by the power meter escaped as usable beam intensity). The concentration of the actinometric solution was adjusted so that no more than about 90% absorption of incident light occurred.

Representative light intensities and absorbed fluxes are as follows. A laser output meter reading of 1 W at 488 nm corresponds to 4×10^{-6} einstein sec^{-1}. In the most favorable case, this impinges on a micropolarimeter cell of window diameter 3 mm to give an intensity of about 6×10^{-5} einstein cm^{-2} sec^{-1} and is absorbed within the 10-cm path length and cell volume of 0.82 cm³ to give an absorbed flux of 5×10^{-3} einstein l.$^{-1}$ sec^{-1}. By contrast, a 1000-W high-pressure Hg lamp provides about 10^{-8} einstein sec^{-1} over a 10-nm band pass, with colimation limited to about 1 cell diameter, so that a 10-cm, 27-cm³ volume spectrophotometer cm would be needed for the irradiation. The corresponding intensity is then 1.3×10^{-8} einstein cm^{-2} sec^{-1} and the flux is 4×10^{-7} einstein l.$^{-1}$ sec^{-1}. The flux figures, which determine the required photolysis times, show the laser source to be as much as 10^4 times faster than the conventional source. It is this performance factor which allows the determination of low quantum yield processes even with systems which undergo moderately fast thermal reactions.

Analytical Procedures. Changes in absorption spectra upon successive irradiations were followed by placing the irradiation cell in the Cary spectrophotometer. In the case of the micropolarimeter cells, a special holder was used; also both the reference and the sample beams were stopped down by means of pinhole apertures since it was found to be important that the latter beam not graze the cell wall.

The isomer ratio of the products from the photolysis of trans-$Co(en)_2Cl_2^+$ was also determined spectrophotometrically. The entire procedure was performed at 0° in order to avoid complications due to thermal aquation. Trace impurities were removed by passing the cold solution of doubly recrystallized trans-$Co(en)_2Cl_2^+$ through an ice-jacketed column containing cold SP-Sephadex C-25 cation exchange resin in the acid form. Several 5-ml aliquots of the complex were photolyzed to only 0.4% photoaquation, made 0.1 M in acid concentration by the addition of 1 M HCl, and then passed through a second Sephadex ion-exchange column. The unreacted trans-$Co(en)_2Cl_2^+$ was eluted with 0.1 M HCl, leaving a blue-violet appearing band of the more highly charged aquation products on the column. The resin containing the products was then removed from the column and the mixture of cis- and trans-$Co(en)_2(H_2O)Cl^{2+}$ extracted into 1.5 M HCl. Using the 10-cm, polarimeter cell, the visible spectrum of the solution was quickly recorded and the product ratio calculated from the absorption data at 490 and 525 nm and published molar extinction coefficient values.[21]

Analysis for released ammonia was by the indophenol spectrophotometric method.[22] The procedure was calibrated with the use of standard ammonium chloride solutions. Photoreleased am-

(13) A. W. Adamson, Proc. Int. Conf. Coord. Chem., 14th (1972).
(14) J. Bjerrum and J. McReynolds, Inorg. Syn., 2, 216 (1946).
(15) H. Diehl, H. Clark, and H. H. Willard, Inorg. Syn., 1, 186 (1939).
(16) F. Basolo and R. K. Murman, Inorg. Syn., 4, 171 (1953).
(17) G. G. Schlessinger, Inorg. Syn., 9, 160 (1967).
(18) M. Krishnamurthy, J. Inorg. Nucl. Chem., 34, 3915 (1972).
(19) B. Bosnich, C. K. Poon, and M. L. Tobe, Inorg. Chem., 4, 1102 (1965).
(20) E. E. Wegner and A. W. Adamson, J. Amer. Chem. Soc., 88, 394 (1966).

(21) M. E. Baldwin, S. C. Chan, and M. L. Tobe, J. Chem. Soc., 4637 (1961).
(22) W. T. Bolleter, C. J. Buchman, and P. W. Tidwell, Anal. Chem., 33, 592 (1961).

Table I

| Complex | Irradiation wavelength, nm | Temp, °C | Other conditions | Quantum yields, ×10⁴ [a] | | | Thermal aquation rate constant, 25° ×10⁶, sec⁻¹ |
				ϕ_{NH_3}	ϕ_{X^-}	$\phi_{Co(II)}$	
Co(NH₃)₆³⁺	488	25	pH 2	3.2 ± 0.3 (6)		<0.035	Very small
	514			2.1 ± 0.05 (3)			
Co(NH₃)₅(H₂O)³⁺	488	25	pH 2	1.8 ± 0.1 (3)		<0.050	Very small
	514			1.3 ± 0.2 (4)			
Co(NH₃)₅F²⁺	488	25	pH 2	19.6 ± 1.5 (5)	5.5 ± 0.3 (4)	<0.38	0.086ᵇ
			pH 4	15.6 ± 0.9 (4)	4.3 ± 0.6 (3)		
			pH 6	20.5 ± 1.2 (4)	4.2 ± 0.7 (3)		
			pH 7	27.5 ± 3.9 (3)	6.8 ± 1.1 (2)		
			pH 8	17.5 ± 1.1 (3)	10.2 ± 4.4 (4)		
			pH 9	19.8 ± 2.6 (4)	9.3 ± 1.4 (3)		
			pH 10	21.5 ± 1.1 (4)	13.7 ± 2.9 (4)		
			pH 11	29.0 ± 2.2 (4)	14.6 ± 2.4 (3)		
Co(NH₃)₅Cl²⁺	488	25	pH 2	50.7 ± 1.3 (3)	17.1 ± 1.2 (3)	1.2	1.7ᵇ
trans-Co(en)₂Cl₂⁺	488	25	pH 2; 0.5 W		10.7 ± 0.3 (3)	1.9	
			pH 2; 0.1 W		10.8 (1)	1.8	32ᶜ
		0	pH 2; 0.6 W		4.9 ± 0.3 (3)		
			pH 2; 0.1 W		4.9 ± 0.1 (2)		
trans-Co(cyclam)Cl₂⁺	488	25	pH 2		4.0 ± 0.1 (7)	<0.1	1.1ᶜ

[a] Numbers in parentheses give the number of independent measurements; the error limits are the average of the magnitudes of the deviations from the average quantum yield values. [b] Halide aquation rates, from ref 29. [c] Chloride aquation rates; see C. K. Poon, *Inorg. Chim. Acta Rev.*, 123 (1970).
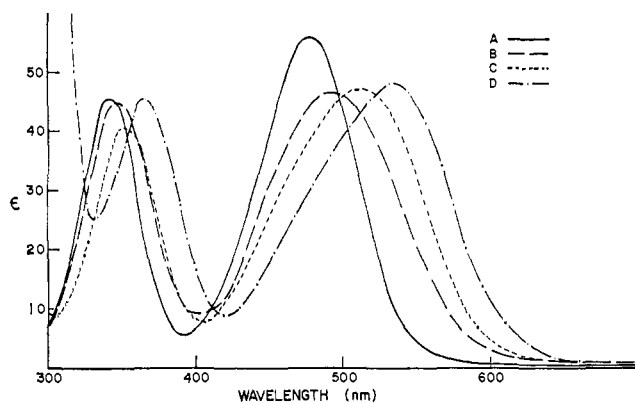

Figure 1. Visible absorption spectra of (A) Co(NH₃)₆³⁺, (B) Co(NH₃)₅(H₂O)³⁺, (C) Co(NH₃)₅F²⁺, and (D) Co(NH₃)₅Cl²⁺.
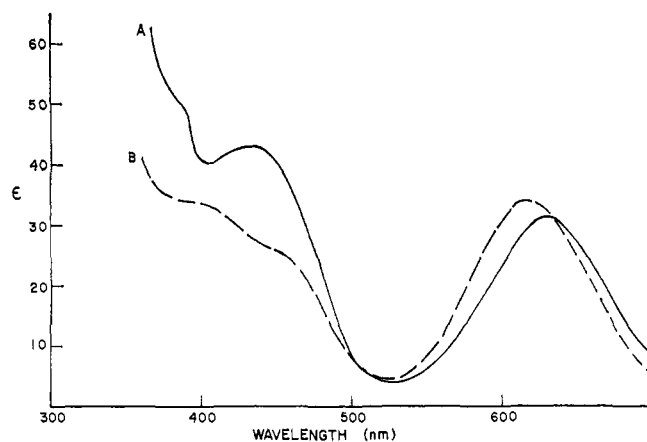

Figure 2. Visible absorption spectra of (A) trans-Co(cyclam)Cl₂⁺ and (B) trans-Co(en)₂Cl₂⁺.

monia was determined from the difference in absorbance at 625 nm of identically treated aliquots of photolyzed and dark solutions.

The procedure of Nichols and Condo[23] was used to determine released fluoride. Again, correction was always made for the dark solution blank. Released chloride was found by titration with mercuric ion using diphenylcarbezone or diphenyl carbazide as end point indicator.[24] The titrant was standardized with known potassium chloride solutions. Mercuric ion catalyzed aquation represented a potential hazard to the method and the complexes present were therefore first removed by passing the solution through an SP-Sephadex C-25 or a Dowex 50 W-X4 cation exchange column, the latter in the acid form. The free chloride present was washed through with 0.01 *M* nitric acid and successive 25-cm³ fractions were titrated until the amount of chloride present receded to the blank value. In all cases 90% of the chloride was recovered in the first fraction.

Cobalt(II) was determined by the method of Kitson,[25] which involves the measurement of the absorption at 625 nm of the Co(II) thiocyanate complex formed in a water–acetone mixture. A reduction, mainly of aquo products, by the thiocyanate present led to a slow increase in Co(II); the absorbance readings were therefore made promptly and extrapolated to the time of mixing of the reagents.

(23) M. L. Nichols and A. C. Condo, Jr., *Anal. Chem.*, **26**, 703 (1954).
(24) F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).
(25) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

Results

Our results are summarized in Table I. The yields ϕ_{NH_3} and ϕ_{X^-} are taken to approximate closely the actual respective photoaquation values. In principle, they should be corrected for the release of ammonia and of halide ion due to the redox mode of photodecomposition; judging from the results of the 254-nm irradiation of Co(III) ammines (see ref 1), we expect either one ammonia or an X⁻ ligand to be oxidized per Co(II) formed and that the remaining ligands would be released to contribute to the apparent photoaquation yields. Our upper limits for $\phi_{Co(II)}$ are small enough, however, that the maximum corrections involved are small and have therefore been omitted.

The absorption spectra of the various complexes are shown in Figures 1 and 2. Note that the irradiation wavelengths used correspond to either the short wavelength side or to the maximum of the L₁ band for the ammonia containing species, while in the case of the dichloro complexes, the wavelength used lies on the long wavelength side of the L₂ band. No large wavelength dependence of the quantum yields is present in
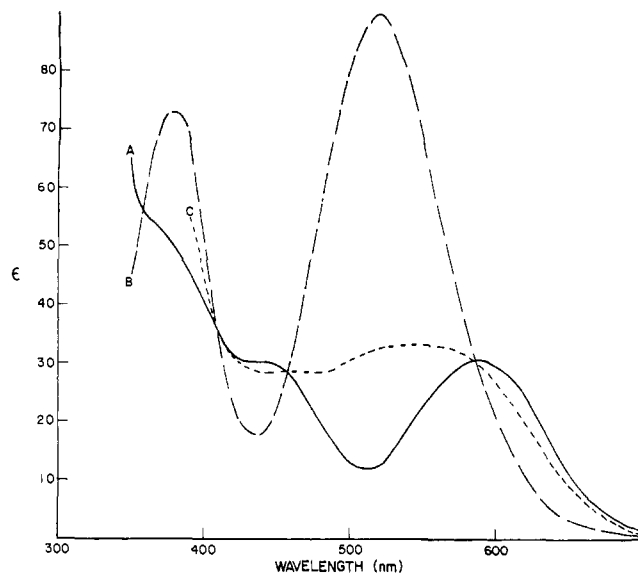
Figure 3. Visible absorption spectra of (A) *trans*-Co(en)$_2$(H$_2$O)Cl^{2+}, (B) *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}, and (C) the products obtained upon photolysis of *trans*-Co(en)$_2$Cl$_2^+$.

the first series, however, although we consider the small decrease with increasing wavelength to be real. The effect is small enough that we will assume that the results for the two sets of complexes are comparable. The temperature dependence of ϕ_{Cl}^- in the case of *trans*-Co(en)$_2$Cl$_2^+$ corresponds to an apparent activation energy of 5.2 kcal mol^{-1} and thus, fairly typically, is in the range of the viscosity activation energy of the solvent. There was no effect of light power on ϕ_{Cl}^- or $\phi_{Co(II)}$ for *trans*-Co(en)$_2$Cl$_2^+$, over the range 0.1 to 0.5 W.

Several additional patterns of behavior may be seen. First, of course, all of the yields are relatively low, but with photoaquation dominant over photoredox decomposition. Second, where both types of ligands are present, ammonia photoaquation is more important than that of X$^-$ by severalfold. Third, the ammonia aquation yields (and perhaps also the Co(II) yields) are significantly larger for the Co(NH$_3$)$_5$X^{2+} complexes than for Co(NH$_3$)$_6^{3+}$ and Co(NH$_3$)$_5$(H$_2$O)$^{3+}$.

Some stereochemical information was obtained concerning the products of the chelate complexes. Successive irradiations of *trans*-Co(cyclam)Cl$_2^+$ produced absorption spectra having an isosbestic point at 608 nm, indicative that essentially only *trans*-Co(cyclam)-(H$_2$O)Cl^{2+} was formed.[26] It was also found that on addition of excess chloride ion following irradiation, the absorption spectrum returned to that of the original complex indicating that neither appreciable isomerization nor decomposition had occurred.

Spectra of a solution of *trans*-Co(en)$_2$Cl$_2^+$, which was similarly irradiated to progressively greater extents of photolysis, maintained the general appearance expected for the generation of mostly *trans*-Co(en)$_2$-(H$_2$O)Cl^{2+}; however, there was no isosbestic point at 490 nm where the molar extinction coefficients of *trans*-Co(en)Cl$_2^+$ and *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} are equivalent, indicating that a second species had been photochemically generated.[21] As a result of a concurrent study

of the photochemistry of *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}, it was realized that the latter complex photoisomerizes with ϕ = 4.2 × 10^{-3}, a factor of ten times greater than that for the photoaquation of *trans*-Co(en)$_2$-Cl$_2^+$.[27] Also, since *cis*-Co(en)$_2$(H$_2$O)Cl^{2+} absorbs more strongly (ϵ 68) than *trans*-Co(en)$_2$Cl$_2^+$ (ϵ 15) at the irradiation wavelength, the combination of these two factors would result in a substantial amount of secondary photolysis if *cis*-Co(en)$_2$(H$_2$O)Cl^{2+} were a major product of the primary photolysis. Even though the over-all photolysis of *trans*-Co(en)$_2$Cl$_2^+$ had been restricted to less than 10%, it was considered a possibility that secondary photolysis might have yielded a product mixture of *cis*- and *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} having a composition which was not representative of the isomer ratio actually produced during the primary photolysis step.

These circumstances indicated that a separate experiment was necessary to determine the percentages of *cis*- and *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} produced directly from the photoaquation of *tran*-Co(en)$_2$Cl$_2^+$. The extent of secondary photolysis was controlled by allowing only 0.4% photoaquation to occur for each of several photolyses required to accumulate a sufficient quantity of aquo products for analysis. As described in the experimental section, the products were isolated on an ion-exchange column and extracted into dilute acid, and the visible spectrum of the solution was recorded. The spectrum of the product solution, shown in Figure 3, is similar to the spectrum reported by Tobe for a mixture of *cis*- and *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} generated thermally in an acidified solution of *trans*-Co(en)$_2$(OH)Cl$^+$.[21]

Since only two possible species were contained in solution, the concentrations were readily determined by the application of Beer's law at 490 nm, where the molar extinction coefficients of *cis*- and *trans*-Co(en)$_2$(H$_2$O)-Cl^{2+} are 72.2 and 14.1, respectively, and 525 nm where ϵ(cis) 89.2 and ϵ(trans) 13.2.[21] After correcting for a small amount (5%) of secondary photolysis, which had occurred even though the photoaquation was restricted to 0.4%, it was determined in this manner that the photolysis of *trans*-Co(en)$_2$Cl$_2^+$ directly produces 72% *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} and 28% *cis*-Co(en)$_2$-(H$_2$O)Cl^{2+},

Discussion

As noted in the introductory section, there are few data in the literature to which we may compare our results. An ammonia aquation yield of 5.2 × 10^{-4} is reported for Co(NH$_3$)$_6^{3+}$ at 472 nm (see ref 1), consistent with the trend we find at somewhat longer wavelengths. An earlier report from this laboratory (see ref 2) gives ϕ_{Cl}^+ as 1.5 × 10^{-3} at 550 nm, for Co(NH$_3$)$_5$Cl^{2+}, somewhat lower than our present observation for 488 nm. No previous photochemistry has been reported for Co(NH$_3$)$_5$F^{2+} or *trans*-Co(cyclam)-Cl$_2^+$ and no ligand field photochemistry for the other complexes except that noted above. The present data thus allow new, if perhaps tentative, conclusions about the ligand field excited state chemistry of Co(III) ammines.

It appears, for example, that the rules for Cr(III)

(26) C. K. Poon, Ph.D. Dissertation, The University College of London, University College, London, England, 1967.

(27) P. S. Sheridan and A. W. Adamson, *J. Amer. Chem. Soc.*, **96**, 3032 (1974).

photolyses[4,28] are mildly applicable. Rules 1 and 2 predict ammonia aquation to be the dominant mode in the cases of $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$ and chloride aquation to be the dominant mode for the *trans*-dichloro complexes, as is observed. The fact that in the first two cases the principal mode is antithermal (only halide aquation being reported for the thermal reaction[29]) indicates that a specific excited state chemistry is involved. The rules are not obeyed as stringently, however, as with the analogous Cr(III) complexes; the ratio ϕ_{NH_3}/ϕ_{Cl^-} is only 3 for $Co(NH_3)_5Cl^{2+}$ while it is about 30 for $Cr(NH_3)_5Cl^{2+}$.[1] Nor do the absolute quantum yields conform well with rule 1; while ϕ_{NH_3} is correctly predicted to be small for $Co(NH_3)_5Cl^{2+}$, it is still 16 times that for $Co(NH_3)_6^{3+}$. The present study does not establish which ammonia photoaquates in an acidopentaammine (a question currently under investigation). If, as one interpretation of the rules suggests (see ref 8), the weak field axis ammonia is the specific one which aquates, then the nature of its axial partner plays some important role. Thus in the series $Co(NH_3)_6^{3+}$, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5Cl^{2+}$, ϕ_{NH_3} increases strongly with decreasing ligand field strength of this partner ($Co(NH_3)_5(H_2O)^{3+}$ is out of line, however).

The smallness of the quantum yield values merits comment. The yields for Co(II) production may be small simply in reflection of a small CT component to the transition involved; alternately, they could reflect a minor level of some hot ground state chemistry. By neither account are the observed yields surprising, but the first explanation would fit the general behavior of the $Co(NH_3)_5X^{2+}$ family in that $\phi_{Co(II)}$ decreases with decreasing intensity of the ligand field bands (and presumed decreasing CT character). (See ref 1 and 2.) There is an interesting alternative possibility, namely that the ligand field state populated has a sufficient lifetime for occasional absorption of a second quantum (to give a CT excited state) to lead to the observed Co(II) yields. A lifetime of about 10^{-6} sec would suffice. This explanation can be ruled out, however, at least in the case of *trans*-$Co(en)_2Cl_2^+$, because of the lack of any intensity effect on $\phi_{Co(II)}$.

The low aquation yields are in contrast to the behavior of many other families of complexes, the most obvious comparison being with those of Cr(III). Some comparative data on Cr(III) complexes are given in Table II. We may express the yield of a photochemical reaction as $\phi_r = \phi'(k_r/(k_r + k_d))$, where ϕ' is the efficiency of formation of the reacting excited state, usually assumed to be a thexi (thermally equilibrated excited) state, and k_r and k_d are the rate constants for reaction and for radiationless deactivation, respectively (emission being negligible in our cases). It may be supposed that the reactive state is not that first obtained and that the population of this reactive state (which might be a triplet or a quintet state in d⁶ ligand field theory) by intersystem crossing is inefficient so that ϕ' is small. Such an intermediary state has been

(28) Rule 1: consider the six ligands to lie in pairs at the end of three mutually perpendicular axes. That axis having the weakest crystal field will be the one labilized, and the total quantum yield will be about that for an O_h complex of the same average field. Rule 2: if the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.

(29) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

Table II

Complex	Irradiation, nm	Temp, °C	ϕ_{NH_3}	ϕ_{X^-}	Ref
$[Cr(NH_3)_6]^{3+}$	320–410 (L_2)	25	0.36		
	380–600 (L_1)	25	0.30		a
$[Cr(NH_3)_5OH_2]^{3+}$	320–700 (L_1, L_2)	25	0.20		
	430–700 (L_1)	26	0.15		a
$[Cr(NH_3)_5Cl]^{2+}$	365 (L_2)	15	0.35	0.05	
	406 (L_2)	1	0.38	0.007	
	506 (L_2)	15	0.36	0.04	
	546 (L_1)	1	0.37	0.005	a
trans-$[Cr(en)_2Cl_2]^+$	400 (L_2)			0.32	
	540 (L_1)			0.35	b
trans-$[Cr(cyclam)Cl_2]^+$	408 (L_2)			0.00079	
	546 (L_1)			0.00069	c

a See ref 1. b A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971). c See ref 3.

invoked recently.[30] This type of explanation is not helpful here since one must still explain why the directly populated state shows no high yield photochemistry. In our cases, k_r must be much less than k_d for either the reacting or for some precursor state, while in the Cr(III) systems $k_r \simeq k_d$. The observation that Co(III) ammines generally do not show low-temperature emission while Cr(III) ones do[31] suggests that it is k_d that has increased rather than k_r that has decreased in going from the former to the latter systems. Our tentative conclusion is that the small aquation yields are more a consequence of enhanced deactivation rates than of reduced excited state chemical reactivity, relative to Cr(III).

Several ligand field analyses of complex ion photochemistry have appeared recently, especially in relation to the Cr(III) family.[5-7] In the more detailed of these Zink places emphasis on the σ and π bonding properties expected for the involved excited state, the language, at least, implying that the determinative chemical consequences can be understood by viewing such effects as acting in the retained geometry of the ground state. Wrighton's approach is similar, with the additional supposition that the excited state bonding changes lead to photoreactivities which are relative to the ground state lability of the complex (thereby implying a communality of mechanism). We have emphasized excited state distortion and the possibility that the reactive thexi state may belong to a different symmetry species than does the ground state and may exhibit a different reaction mechanism.[32]

The probable importance of excited state mechanism is suggested by the following comparisons between our systems and the corresponding Cr(III) ones. First, the photoaquation of *trans*-$Co(en)_2Cl^{2+}$ is largely stereoretentive (and thus copies the thermal reaction), in contrast to *trans*-$Cr(en)_2Cl^{2+}$ which gives primarily *cis*-$Cr(en)_2(H_2O)Cl^{2+}$,[8-10] (and is antithermal). Second, ϕ_{Cl^-} is about the same for *trans*-$Co(en)_2Cl_2^+$ as for *trans*-$Co(cyclam)Cl_2^+$, reactions of the same basic stereochemistry, while in the case of the Cr(III) complexes a 1000-fold reduction in yield occurs, but with the *trans*-$Cr(cyclam)Cl_2^+$ now giving *trans*-$Cr(cyclam)(H_2O)Cl^{2+}$,[3]

(30) N. A. P. Kane-Maguire and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 351 (1972).

(31) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

(32) A. W. Adamson, *Pure Appl. Chem.*, **20**, 25 (1969).

so that reactions of different stereochemistry are being compared. It would appear that for Co(III) ammines expulsion of the labilized ligand occurs without being affected to any great degree by rigidity imposed by the ligands, to yield predominantly stereoretentive products, while the usual high quantum yields for Cr(III) ammines are found only if stereolability is geometrically feasible, which suggests a more concerted process.

The thermal reaction chemistry of a complex does not constitute a good guide to its photochemical behavior. The thermal chemistry does not predict antithermal reactions, of course. Further, $Co(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ have much more similar thermal aquation rates, 1.7×10^{-6} and 7.3×10^{-6} sec^{-1}, at 25°, than photoaquation yields, even comparing only the ϕ_{Cl^-} values. Also, the 25° rate constants for chloride aquation are 3.2×10^{-5} and 2.4×10^{-5} M^{-1} sec^{-1} for trans-$Co(en)_2Cl_2^+$ and trans-$Cr(en)_2Cl_2^+$, respectively, or about the same, while the ϕ_{Cl^-} values differ by a factor of about 300. Finally, as seen in Table I, within the Co(III) acidoammine series there is no parallel between thermal aquation rate constants and quantum yields. By contrast, and curiously, such a parallel is present in the series trans-$CrLCl_2^+$, where L denotes $4NH_3$, 2 en, 2,3,2-tet, or cyclam,[33] even though the stereochemistries of the photo and thermal reactions are different in the first three cases.

It is our present feeling that while empirical photolysis rules are useful, ligand field theoretical rationalizations of such rules must be viewed with caution until radiationless deactivation rates, thexi state distortions, and detailed excited state mechanisms can be included. We

believe all of these factors to be important in Co(III) and Cr(III) photochemistry.

The effect of pH on the photolysis of $Co(NH_3)_5F^{2+}$ was studied with two possibilities in mind. Co(III) acidopentaammines are well known to undergo base-catalyzed aquation, probably through a counter-base mechanism.[29] One possibility was that the excited state responsible for aquation would have a sufficiently lower pK_a for hydroxide-catalyzed aquation to set in at lower pH's than for the thermal reaction. Alternatively, even a small degree of ground state deprotonation might produce a sufficiently photoactive species for a significant increase to occur in our low-aquation yields.

There is sufficient scatter in the values for ϕ_{NH_3} that no firm trend with pH can be claimed. The values for ϕ_{F^-}, however, do show a regular increase with pH, leveling off at pH 10 to about three times the value for acid solutions. Such leveling off would not occur if a ground state deprotonation were involved; pK_a of the ground state is large enough that no saturation effect is expected (or observed in the thermal base-catalyzed aquation reaction). We therefore assign the pH dependence of ϕ_{F^-} to an excited state acid–base equilibrium, the pK_a for which appears to be about 8 (the mid-point pH for the quantum yield change). The effective reactivity of the counter-base form of the excited state is evidently not much greater than that of the acid form, either because of little change in k_d and k_r or because of parallel changes in both rate constants.

(33) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).

Photochemistry of Complex Ions. XIII.
cis-[Co(en)₂Cl₂]⁺ and cis-[Co(en)₂(H₂O)Cl]²⁺

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Abstract: The ligand field photolysis of cis-[Co(en)₂Cl₂]⁺ in acidic solution is shown to consist of chloride aquation ($\Phi = 0.0024$) to yield 70 to 75% trans-[Co(en)₂(H₂O)Cl]²⁺ and 25 to 30% cis-[Co(en)₂(H₂O)Cl]²⁺, after correction for secondary photolysis of the latter species. This species undergoes cis to trans isomerization with $\Phi = 0.0042$, while the trans isomer is photoinert. Quantum yields for other processes such as ethylenediamine aquation, second chloride aquation, or redox decomposition are entirely negligible. The photoinduced stereochemical rearrangements are antithermal in nature, and they are discussed in terms of the photolysis rules which have been used for Cr(III) complexes.

W̶e pursue in this paper the ligand field photochemistry of cis-[Co(en)₂Cl₂]⁺ and cis-[Co(en)₂(H₂O)Cl]²⁺ as part of a developing interest in the nonredox photochemistry of Co(III)–ammine complexes. The preceding paper[1] reports observations on the compounds [Co(NH₃)₅X]ⁿ⁺ (X = NH₃, H₂O, F⁻, and Cl⁻), trans-[Co(en)₂Cl₂]⁺, and trans-[Co(cyclam)Cl₂]⁺. In general,

irradiation of the first or second ligand field bands (L_1 and L_2) caused ligand aquation, although at a low level of absolute quantum yield. Due to the choice of the non-ammine ligands, and the irradiation wavelength (no charge-transfer absorption), complications due to photoinduced redox decomposition were minimal, and the photochemistry could be interpreted in terms of the photolysis rules used for Cr(III) complexes.[2]

(1) (a) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Amer. Chem. Soc.*, **96**, 3027 (1974); (b) A. W. Adamson, *Proc. Int. Conf. Coord. Chem., 14th* (1972).

(2) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).